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Predicted Characteristics of Waste Materials From the Processing of Manganese Nodules

By Benjamin W. Haynes and Stephen L. Law

UNITED STATES DEPARTMENT OF THE INTERIOR

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UNITED STATES DEPARTMENT OF THE INTERIOR
James G. Watt, Secretary

BUREAU OF MINES
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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

cm/sec	centimeters per second	ng/g	nanograms per gram	pcf	pounds per cubic foot
µg/g	micrograms per gram	pct	percent	psi	pounds per square inch
µm	micrometer	pg/g	picograms per gram	wt-pct	weight-percent

PREDICTED CHARACTERISTICS OF WASTE MATERIALS FROM THE PROCESSING OF MANGANESE NODULES

By Benjamin W. Haynes[1] and Stephen L. Law[2]

ABSTRACT

As part of the first-order assessment of potential manganese nodule processing reject waste materials, the Bureau of Mines estimated the physical and chemical characteristics of reject waste materials that would be generated from each of five potential process flowsheets. These processes were chosen because of their economic and technical feasibility for first-generation nodule processing. A brief description of the five processes is given to show process inputs and outputs. The physical characteristics are predicted based on land-based laterite processing where applicable, and where no land-based analog exists, on the basis of process chemistry. The probable chemical characteristics such as element content and compound form are tabulated for each process for 16 elements: As, Ba, Be, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, Tl, and Zn. These elements were chosen based on their presence on the toxic substance list of priority pollutants, EP toxicity criteria, and major and minor elements of economic importance (Co, Fe, Mn, and Mo).

Physical and chemical analyses as well as results of the EP toxicity test of one industrially supplied pilot plant reject waste material are presented.

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INTRODUCTION

This report is the initial effort of the Bureau of Mines to document the results of a research project entitled "Analysis and Characterization of Manganese Nodule Processing Rejects." Deep seabed mining for manganese nodules, including the processing of nodules to recover value metals, raises a variety of environmental, social, and economic considerations. To address the waste management aspects of the recovery of value metals from nodules, the National Oceanic and Atmospheric Administration (NOAA) of the Department of Commerce, the Environmental Protection Agency (EPA), and the Department of the Interior's Bureau of Mines and Fish and Wildlife Service, after consultation with affected and concerned interests, have agreed to embark on a multiyear cooperative research program which has the following overall objective:

> "To provide information needed by Federal and State agencies in preparation for receipt of industry's commercial waste management plans."

Under the Deep Seabed Hard Mineral Resources Act of 1980 (PL 96-283), NOAA has been designated as the lead agency in developing terms, conditions, and restrictions for the proposed mining of nodules and for the disposal of wastes. The NOAA-funded research conducted by the Bureau has the objective of obtaining a "first-order chemical and physical characterization of rejects from the types of manganese nodule processing techniques representative of those being developed by industry." The final product of this research will be a technical report that can be used by (a) industry and environmental scientists in subsequent research to assess the potential effects of waste management alternatives; and (b) regulatory agencies in the determination of the standards and test requirements to be met. This is expected to facilitate the development of a basic framework that accommodates the desire to assure good waste management practices and assist in the development of a new minerals processing industry.

To meet the objective of characterization of the reject waste material from the several potential first-generation process schemes, a knowledge of the nodule feed material and the processes considered feasible for first-generation processing plants is necessary. A report has been prepared describing the mineralogical and elemental characteristics of Pacific manganese nodules (*7*).[3] A second report describing the five most feasible process flowsheets for first-generation plants has also been prepared (*6*). Based on the information in these two reports, this report predicts the physical and chemical characteristics of manganese nodule reject waste material for each of the five processes. Other types of wastes

[3] Italicized numbers in parentheses refer to items in the list of references at the end of this report.

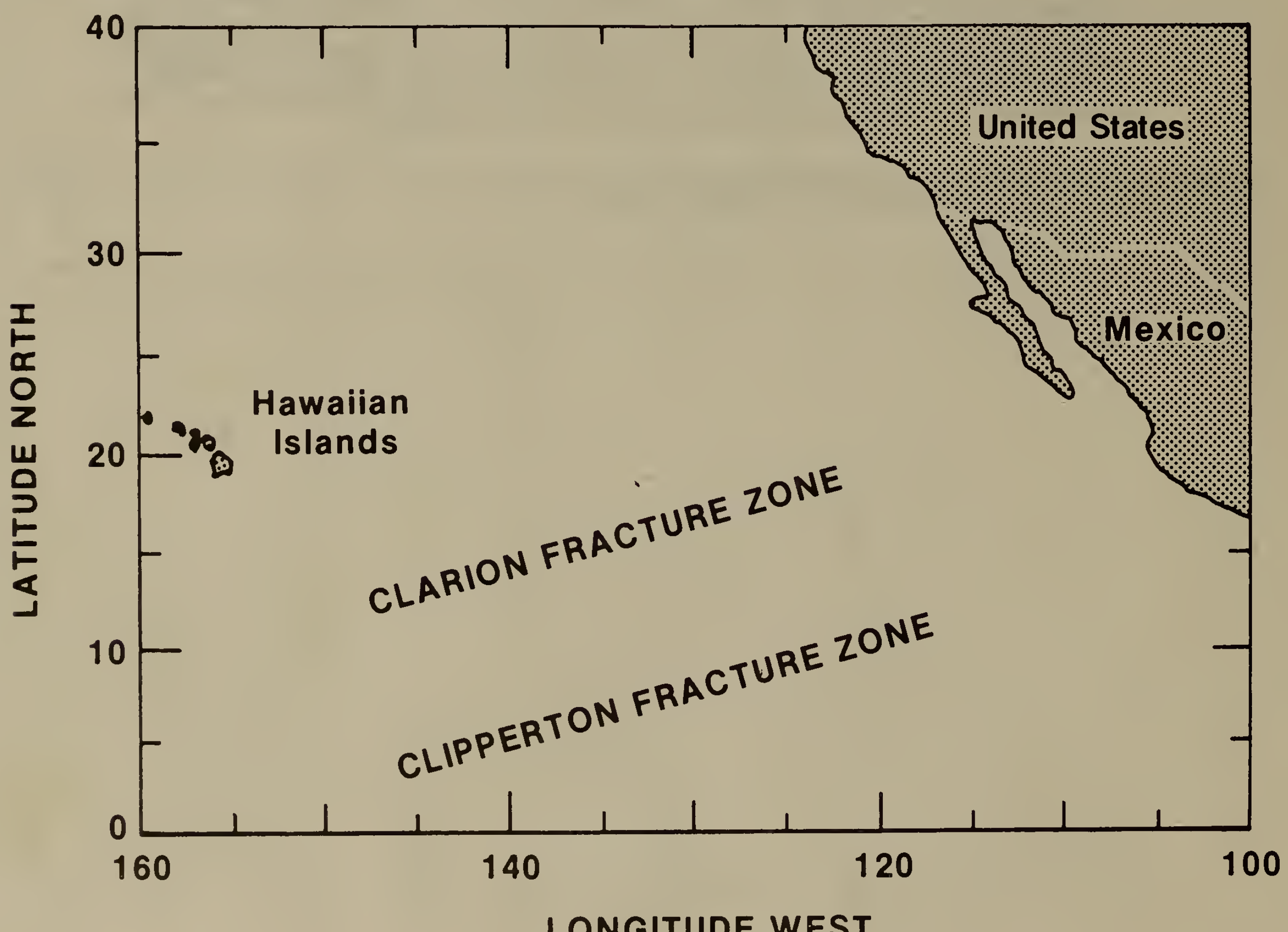

Figure 1.—Area of prime interest for first-generation nodule mining, Clarion-Clipperton Fracture Zone area.

generated in these processes, such as scrubber sludges, flyash, and electrowinning sludges, are not included in this report. These wastes constitute only a small fraction (<15 pct) of the total wastes generated for the processes considered in this report, have compositions that are generally well established, and have been detailed in a previous report (*2*).

Based on available information, the area of prime interest for first-generation nodule mining is that area between the Clarion and Clipperton Fracture Zones (CC-zone area) of the northeast equatorial Pacific shown in figure 1. Table 1 gives the composition of CC-zone area nodules based on available data (*7*). The predictions of physical and chemical characteristics for the five processes will be based on CC-zone area nodule composition.

The types of processes considered most technically feasible for first-generation nodule processing are as follows:

1. Gas reduction and ammoniacal leach.
2. Cuprion ammoniacal leach.
3. High-temperature and high-pressure sulfuric acid leach.
4. Reduction and hydrochloric acid leach.
5. Smelting and sulfuric acid leach.

The two ammoniacal and the high-temperature and high-pressure sulfuric acid processes are designed to recover three metals (Co, Cu, and Ni) and the other two processes are designed to recover four metals (Co, Cu, Ni, and Mn).

Each process waste will be discussed in two sections, one dealing with physical characteristics and the other dealing with chemical characteristics. In the chemical characteristics section, the elements discussed are the following 18 elements of potential economic and/or environmental interest: Ag, As, Ba, Be, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, Tl, and Zn. Thirteen of these elements were chosen because they are listed as priority pollutants under the Toxic Substance Control Act of 1976 (PL 94-469). Cobalt, iron, manganese, and molybdenum are included because they are major constituents of nodules and/or are of economic importance; and barium is included because of its presence on the EPA list of leachable metals in the Extraction Procedure (EP) toxicity test (*4-5*). Based on the information in the report on the mineralogical and elemental description of Pacific nodules (*7*), the concentration level for each of the 18 elements in Pacific nodules for the CC-zone area is given in table 1.

EPA listed levels for eight extractable metals in its EP toxicity test (*4-5*). If the leachate of a material subjected to this procedure contains Ag, As, Ba, Cd, Cr, Hg, Pb, and/or Se at 100 times the National Drinking Water Standard, that waste is considered hazardous under the toxicity definition. In order for a material to exceed these limits for mercury and silver, it must contain 4 μg/g and 100 μg/g of mercury and silver respectively; and all must be leachable. Concentrations of these two elements are well below those upper limits in all manganese nodules. In order for mercury or silver to exceed this limit, they must be concentrated during processing by factors of 50 and 2,500 respectively. Because only a small, if any, concentration factor is involved in the five processes, it is extremely unlikely that the levels could be attained. The remaining 16 elements will be discussed in each process section.

In considering the processing of nodules, the three major mineral phases subject to attack by the lixiviant are the manganese, iron oxide, and accessory mineral phases. All lixiviants used in the four hydrometallurgical processes are selected for maximum extraction of Co, Cu, and Ni from the manganese and iron oxide mineral phases except for HCl which also extracts manganese. This implies that the minerals and elements in the accessory mineral phase are only unintentionally modified from the form in which they originally occur in the nodules. The elements associated with this accessory mineral phase are Al, K, Na, Si, and possibly Cr and Zr. For the smelting process, all phases of the nodule are affected.

Table 1.—Composition of Clarion-Clipperton Fracture Zone area Pacific manganese nodules

Element	Mean	Median	Element	Mean	Median
Aluminum ... pct..	2.9	2.5-3.0	Molybdenum ... pct..	0.052	0.050-0.060
Antimony ... μg/g..	37	36	Neodymium ... μg/g..	159	138
Arsenic ... μg/g..	159	164	Nickel ... pct..	1.28	1.30-1.40
Barium ... pct..	0.277	0.200-0.220	Niobium ... μg/g..	74	80
Beryllium ... μg/g..	4	2	Nitrogen (NO_3^-) ... μg/g..	560	400
Bismuth ... μg/g..	21	23	Palladium ... ng/g..	6.2	6.3
Boron ... μg/g..	273	221	Phosphorus (P_2O_5) ... μg/g..	2,300	2,100
Bromine ... μg/g..	500	500	Platinum ... ng/g..	97	110
Cadmium ... μg/g..	12.3	10-15	Potassium ... pct..	1.01	0.80-0.90
Calcium ... pct..	1.7	1.5-2.0	Praseodymium ... μg/g..	36	34
Carbon ... pct..	0.19	0.19	Radium ... pg/g..	8.5	5.1
Cerium ... μg/g..	532	340	Rhenium ... μg/g..	<0.2	INS
Cesium ... μg/g..	0.75	<0.7	Rubidium ... μg/g..	15	15
Chlorine ... pct..	0.53	0.78	Ruthenium ... ng/g..	18	INS
Chromium ... μg/g..	27	15-20	Samarium ... μg/g..	35	32
Cobalt ... pct..	0.24	0.20-0.30	Scandium ... μg/g..	10	10
Copper ... pct..	1.02	1.00-1.10	Selenium ... μg/g..	52	53
Dysprosium ... μg/g..	31	32	Silicon ... pct..	7.6	6.0-6.5
Erbium ... μg/g..	20	23	Silver ... ng/g..	101	39
Europium ... μg/g..	8	7	Sodium ... pct..	2.79	2.00-2.25
Fluorine ... μg/g..	130	<100	Strontium ... pct..	0.045	0.040-0.050
Gadolinium ... μg/g..	32	32	Sulfur ($SO_4^{=}$) ... pct..	1.84	0.40
Gallium ... μg/g..	11	6	Tantalum ... μg/g..	11	11
Germanium ... μg/g..	42	37	Tellurium ... μg/g..	216	214
Gold ... ng/g..	1.93	1.92	Terbium ... μg/g..	5.4	5
Hafnium ... μg/g..	6	5	Thallium ... μg/g..	169	160
Holmium ... μg/g..	4	4	Thorium ... μg/g..	28	21
Iodine ... μg/g..	510	230	Thulium ... μg/g..	2.3	2
Iridium ... ng/g..	9.1	4.3	Tin ... μg/g..	108	80
Iron ... pct..	6.9	6-7	Titanium ... pct..	0.53	0.40-0.50
Lanthanum ... μg/g..	160	135	Tungsten ... μg/g..	76	80
Lead ... pct..	0.045	0.040-0.050	Uranium ... μg/g..	6.8	5
Lithium ... μg/g..	160	100	Vanadium ... pct..	0.047	0.040-0.050
Lutetium ... μg/g..	1.8	2	Ytterbium ... μg/g..	20.5	18
Magnesium ... pct..	1.65	1.50-1.75	Yttrium ... μg/g..	133	111
Manganese ... pct..	25.4	26-27	Zinc ... pct..	0.14	0.10-0.15
Mercury ... ng/g..	152	85	Zirconium ... pct..	0.035	0.030-0.040

INS Insufficient data for median.

In the five processes, three lixiviants are used: ammonia-ammonium carbonate in the two ammonia leach processes, sulfuric acid in the sulfuric acid process and the smelting process, and hydrochloric acid in the hydrochloric acid process. The major anion combining forms for the elements are carbonate ($CO_3^=$), sulfate ($SO_4^=$), and chloride (Cl^-), respectively. Therefore, most compounds present in the tailings would be a form of one of the preceding anions (depending on process type), an oxide or hydroxide, and/or remain unaltered from the original nodule feed material (for example, silicates).

The predictions of physical and chemical characteristics made in this report are based on limited data from other sources (*2*), process flowsheets and anticipated reactions, solubilities, efficiencies obtained in tailings washings, and, in the case of Cuprion tailings, information obtained on pilot plant-generated material. Some estimates are subjective, reflecting the authors' conception of the process. The values reported therefore are estimates only and should not be construed as necessarily representing the composition of any tailings that will be produced in a full-scale plant.

PROCESS DESCRIPTIONS

Each of the five processes considered as feasible for first-generation manganese nodule processing is presented in abbreviated form. More thorough discussions of these processes are given elsewhere (*2, 6*).

GAS REDUCTION AND AMMONIACAL LEACH PROCESS

The gas reduction and ammoniacal leach process is a three-metal process in which Cu, Ni, and Co are liberated by an oxidizing ammonia-ammonium carbonate leach following the high-temperature reduction of manganese dioxide by synthesis gas. Copper and nickel are coextracted by liquid ion exchange reagents and are selectively stripped and recovered by electrowinning. Cobalt is separated from the raffinate by precipitation with hydrogen sulfide and is recovered from the sulfide precipitate, along with some Ni, Zn, and Cu, by selective leaching and hydrogen reduction. The metal-free raffinate is recycled to provide leach liquor and for washing tailings from the process. Ammonia and ammonium carbonate are recovered from leach tailings by steam stripping. A simplified block diagram of this process is shown in figure 2. This process is an adaptation of the Caron process presently used on nickel laterites at Nicaro, Cuba, and Greenvale, Australia (*1, 8*). The major differences between the nodule process and the Caron laterite process are the methods of metal separation and purification.

CUPRION AMMONIACAL LEACH PROCESS

The Cuprion process is a three-metal process in which Co, Cu, and Ni are liberated in an ammonia-ammonium carbonate leach following a reduction-leach step. Carbon

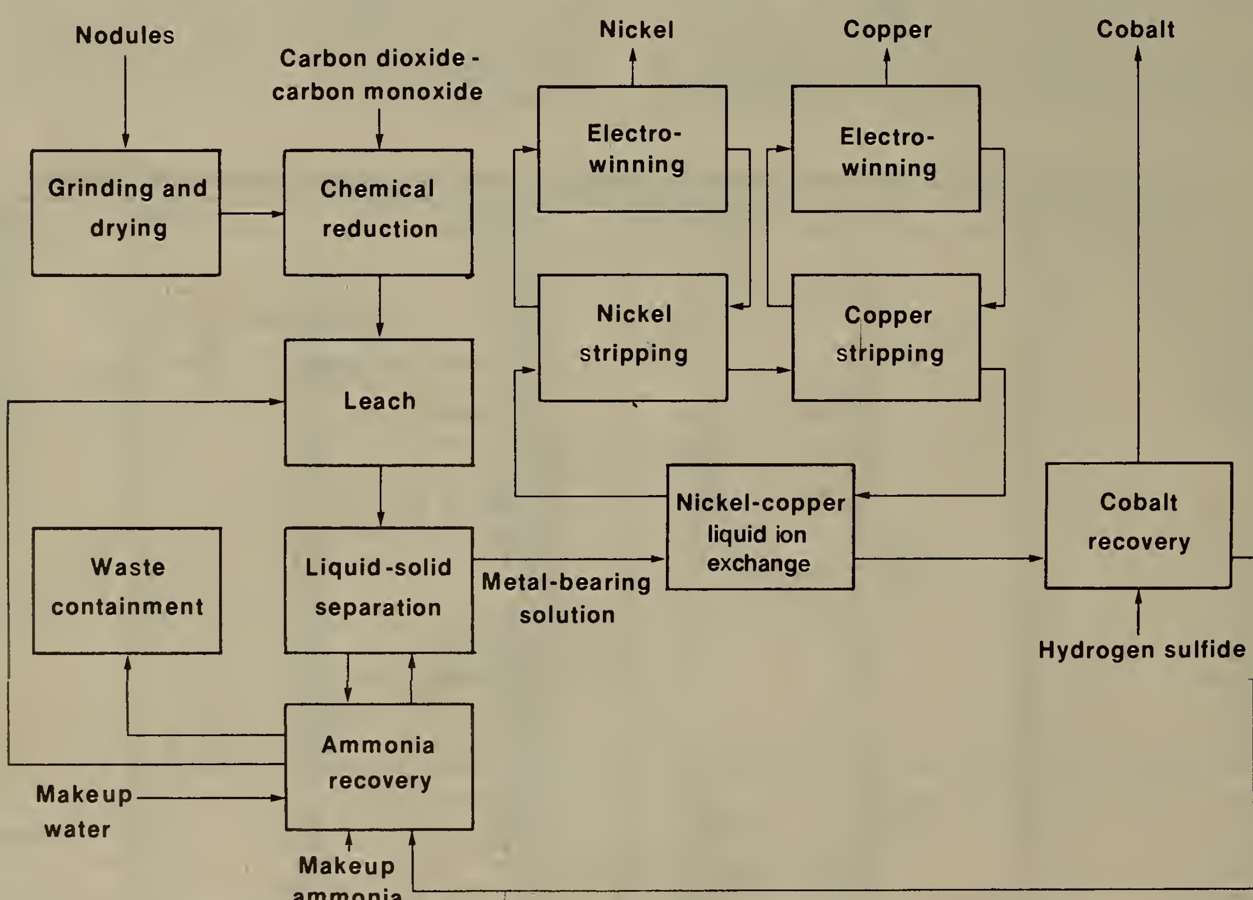

Figure 2.—Gas reduction and ammoniacal leach process.

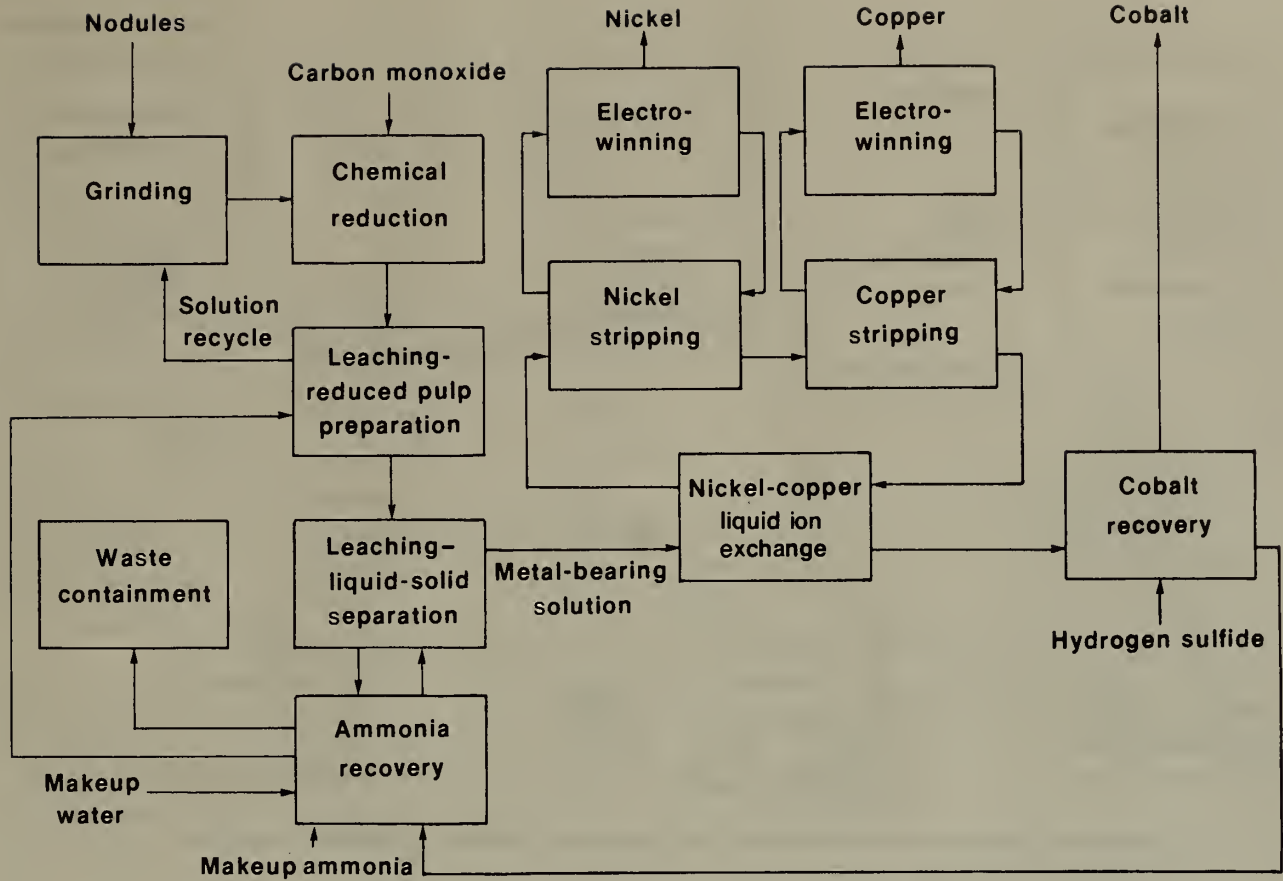

Figure 3.—Cuprion ammoniacal leach process.

monoxide is used to regenerate the cuprous ion which reduces the manganese dioxide. Copper and nickel are coextracted by liquid ion exchange reagents and are selectively stripped and recovered by electrowinning. Cobalt is separated from the raffinate by precipitation with hydrogen sulfide and is recovered from the sulfide precipitate along with some Ni, Zn, and Cu, by selective leaching and hydrogen reduction. The metal-free raffinate is steam stripped to recover a high-strength ammonia solution for recycle to the tailings wash step, together with ammonia and ammonium carbonate recovered by steam stripping the leach tailings. A simplified block diagram of this process is shown in figure 3. This process is similar to the Caron process used for nickel laterites except that the reduction is done at ambient temperature by an aqueous-solid reaction instead of gas reduction, and the methods of metal separation and purification are different.

HIGH-TEMPERATURE AND HIGH-PRESSURE SULFURIC ACID LEACH PROCESS

The high-temperature and high-pressure sulfuric acid leach process is a three-metal process in which Co, Cu, and Ni are selectively leached from the nodules by strong sulfuric acid at high temperature and pressure. After separation of the nodule residue from the leach solution, the copper and nickel are coextracted by liquid ion exchange reagents and selectively stripped and recovered by electrowinning. Cobalt is separated from the raffinate by precipitation with hydrogen sulfide and is recovered from the sulfide precipitate, along with some Cu, Ni, and Zn, by selective leaching and hydrogen reduction. The metal-free raffinate liquor is recycled to the washing process. Ammonia consumed in the process is recovered and recycled to the process for use in pH control. A simplified block diagram of this process is shown in figure 4. A basically similar process for treating nickel laterites has been used at Moa Bay, Cuba (*3*), except that the metal separation and purification procedures are different.

REDUCTION AND HYDROCHLORIC ACID LEACH PROCESS

The hydrochloric acid process is a four-metal process in which Co, Cu, Mn, and Ni are liberated from dried nodules by a high-temperature (500° C) gaseous hydrogen chloride treatment of nodules. Hydrogen chloride reduces manganese dioxide to manganous chloride (liberating chlorine gas) and also reacts with other metal oxides to form soluble chloride salts. A hydrolysis reaction and quench follow, where water is sprayed on the nodules and the iron is precipitated as ferric hydroxide. The nodules are leached with aqueous hydrochloric acid, forming a concentrated pregnant liquor of chloride salts. Copper is extracted by liquid ion exchange reagents from the pregnant liquor, stripped, and recovered by electrowinning. Cobalt is extracted from the copper raffinate by liquid ion exchange reagents, stripped, separated by precipitation with hydrogen sulfide, and is recovered from the sulfide precipitate, along with some Cu, Ni, and Zn, by selective leaching and hydrogen reduction. Nickel is extracted by liquid ion exchange reagents from the cobalt raffinate, stripped, and recovered by electrowinning. The nickel raffinate is evaporated crystallizing manganese chloride as well as the other remaining chloride salts. The salts are dried using combustion gases in a countercurrent dryer. The dried salts are charged to a high-temperature fused salts electrolysis furnace, where molten manganese metal is tapped and cast as product and

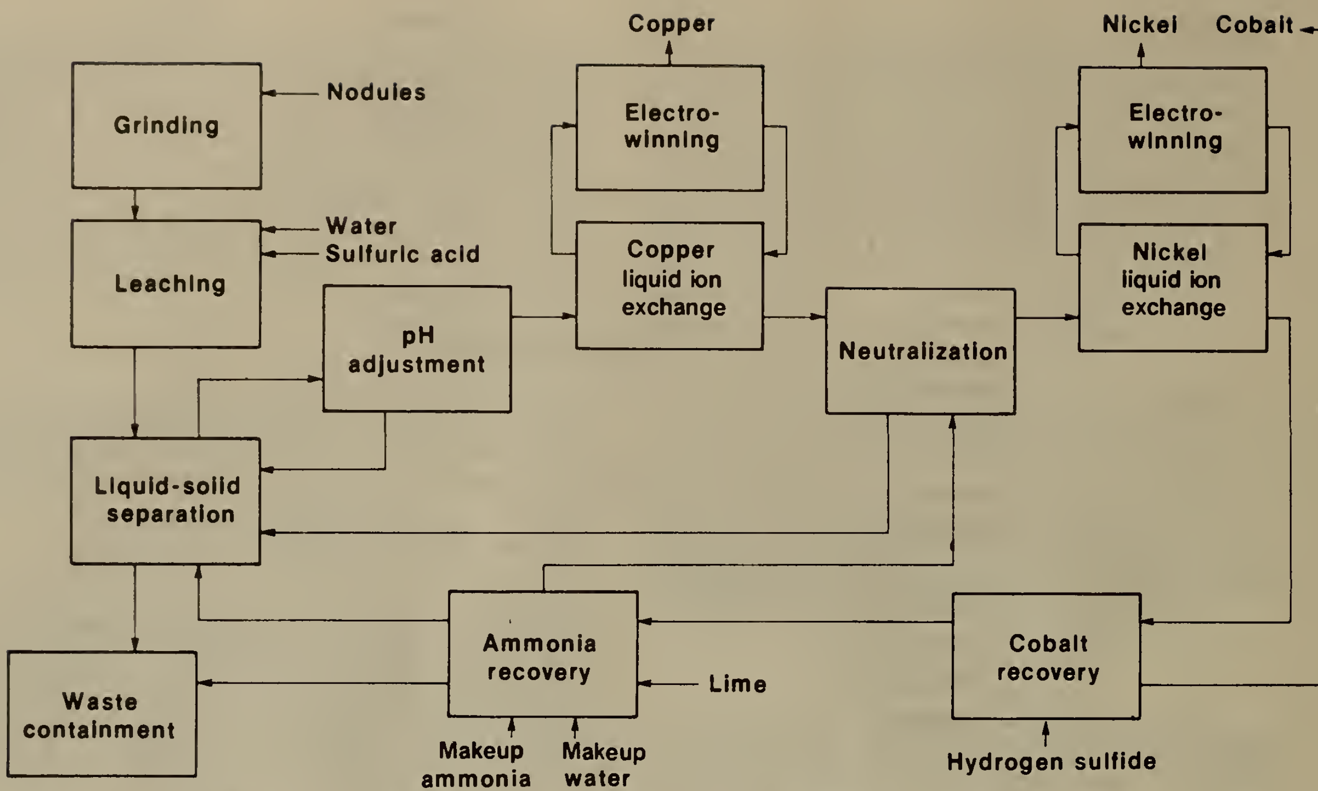

Figure 4.—High-temperature and high-pressure sulfuric acid leach process.

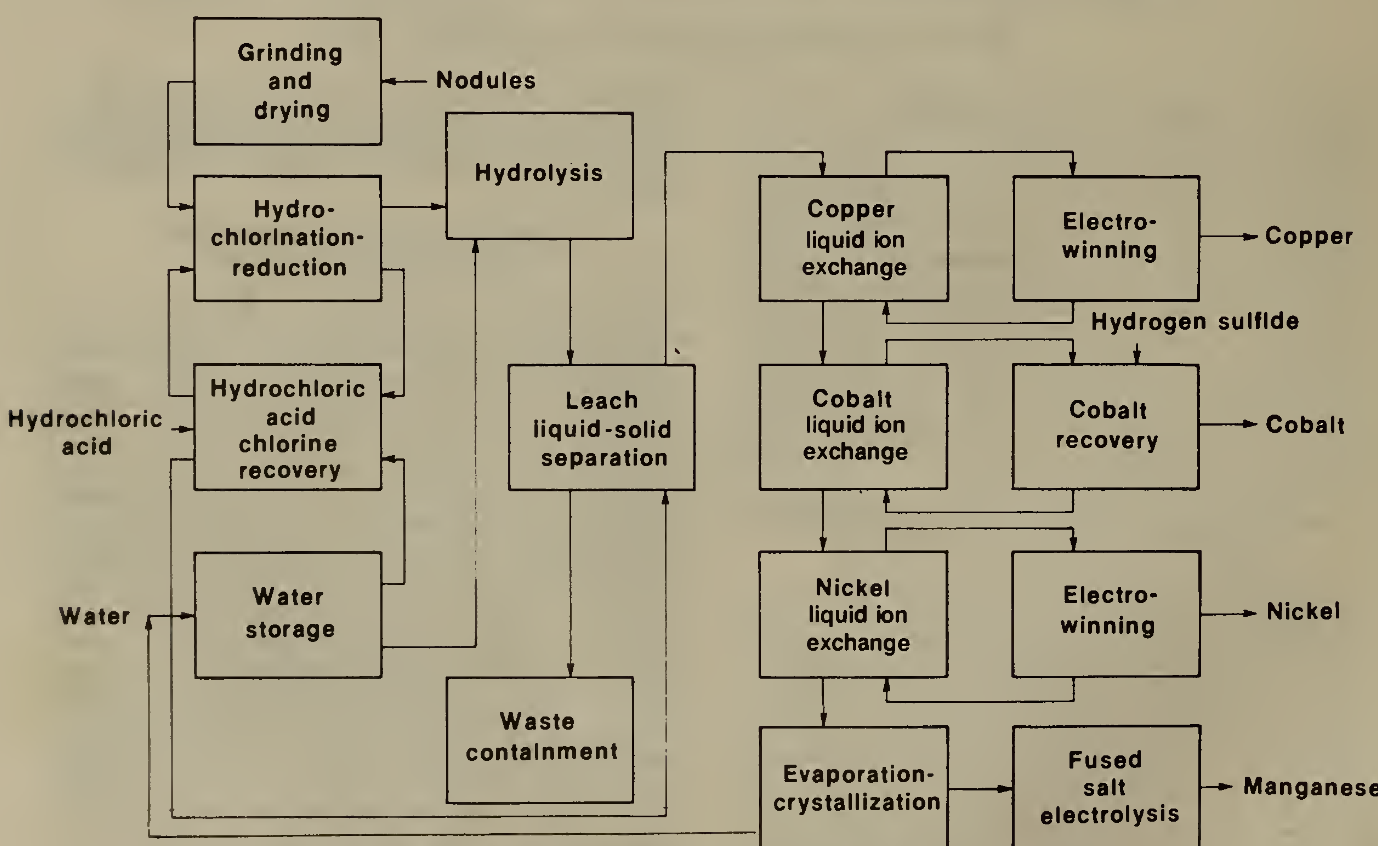

Figure 5.—Reduction and hydrochloric acid leach process.

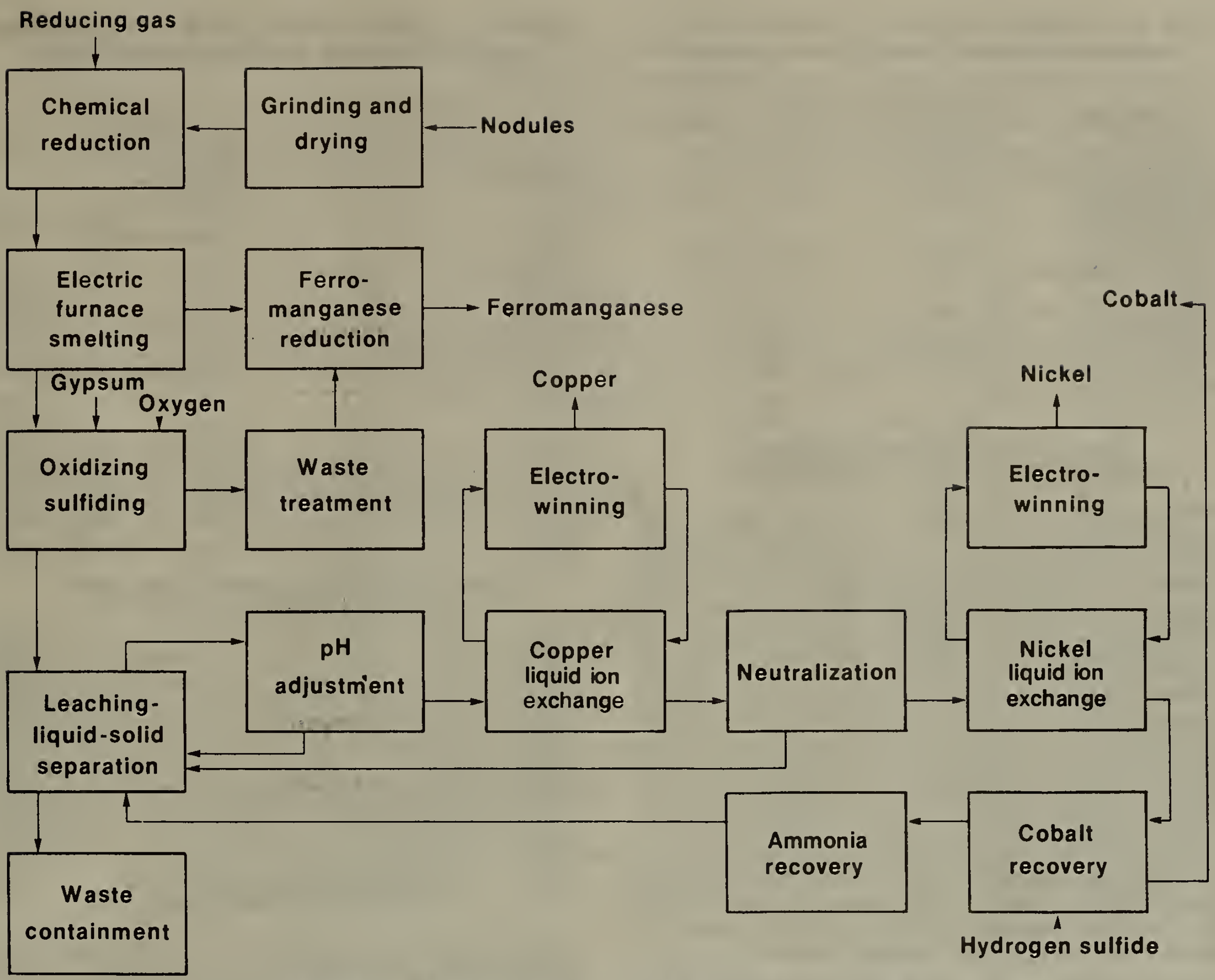

Figure 6.—Smelting and sulfuric acid leach process.

chlorine gas is liberated. Excess hydrogen chloride gas in the process is recovered and recycled. Generated chlorine gas is recovered, dried, and delivered to a local chemical complex which, in exchange, returns makeup hydrogen chloride to the process. This process has no direct analog in existing ore processing. A simplified block diagram of this process is shown in figure 5.

SMELTING AND SULFURIC ACID LEACH PROCESS

The nodule smelting process is a combination pyrometallurgical and hydrometallurgical treatment of nodules to recover the value metals, Co, Cu, and Ni, with the option of recovering ferromanganese. The smelting process produces a slag from which ferromanganese is recovered and a matte composed primarily of Co, Cu, Ni, and S. The matte is granulated, slurried, and selectively leached with sulfuric acid at elevated temperature and pressure (*9*). The leach residue and metalliferous solution are separated by a series of filtering and washing stages. After liquid-solid separation, copper and nickel are selectively extracted by liquid ion exchange, stripped from the ion exchange liquid into a depleted electrolyte, and recovered by electrowinning. Cobalt is separated from the raffinate by precipitation with hydrogen sulfide and is recovered from the sulfide precipitate, along with some Cu, Ni, and Zn, by selective leaching and hydrogen reduction. Ammonia consumed in the process is recovered by lime boil and is recycled to the process for use in pH control. A simplified block diagram of this process is shown in figure 6. The reject waste material in this process consists of slags that are produced during smelting and refining and a small amount (~1 pct) of tails from sulfide matte leaching. Many industrial analogs are available for nonferrous smelting processes. The physical characteristics of nodule reject slags are expected to be similar to those of glassy, inert slags from present smelting operations, whereas the chemical characteristics may differ.

PHYSICAL CHARACTERISTICS

The predicted physical characteristics for the five selected processes are presented in four groups. Because of similarities between the gas reduction and Cuprion ammoniacal leach processes, they are discussed together; the other three are discussed separately. Presented in the ammoniacal leach processes section is an analysis of a pilot plant-generated Cuprion waste. Table 2 is a summary of the predicted physical properties of the reject waste materials.

Table 2.—Predicted physical characteristics of manganese nodule reject waste material

Process type	Settling density, pct solids	Grain size, mesh	Stability
Gas reduction and Cuprion ammonical leach process.	50-60	−200	Good.
High-temperature and high-pressure sulfuric acid leach process.	40-50	−200	Good.
Reduction and hydrochloric acid leach process.	30-50	−270	Fair.
Smelting and sulfuric acid leach process.[1]	NAp	>10	Excellent.

NAp Not applicable (dry inert slags).
[1] Does not include leach residues from sulfide leaches which comprise only about 1 pct of the waste material.

Table 3.—Physical composition of Cuprion pilot plant-generated reject waste material[1]

Parameter	Results
Grain size distribution	100 pct pass 74 μm. 50 pct pass 6 μm.
Specific gravity	3.19 (dry solids).
Triaxial shear	38° friction angle. 5 psi cohesion.
Permeability	8.46×10^{-6} cm/sec at 95 pct maximum density.
Maximum density ... pcf..	90.1
Atterberg limits:	
Liquid ... pct..	45
Plastic ... pct..	41.2
Soil class..	ML (lean silt).
Slurry density ... wt-pct..	41.8

[1] Analysis provided by R. W. McKibbin, mining engineer, Spokane (Wash.) Research Center.

GAS REDUCTION AND CUPRION AMMONIACAL LEACH PROCESSES

The physical characteristics of nodule reject waste material from the gas reduction and Cuprion ammoniacal leach processes are expected to be similar to those of nickel laterite tailings generated by the Caron process. These wastes from laterite processing settle to relatively high densities and become a mechanically stable waste. The major difference between the laterite tailings and manganese nodule tailings would be the relative iron and manganese contents. Laterite tailings are higher in iron and lower in manganese, while nodule tailings will be of an opposite composition. This iron-to-manganese ratio should have little effect on the physical parameters of the respective tailings. Typical physical characteristics of these tailings would be a particle size of minus 200 mesh, settling densities of 50 to 60 pct (percent solids), and good long-term stability (*1, 8*).

Table 3 gives the analysis of a pilot plant-generated reject waste material as reported by the Bureau's Spokane (Wash.) Research Center. These results may not be typical of final rejects produced during full-scale plant operation because of variances that occur during pilot plant operation.

HIGH-TEMPERATURE AND HIGH-PRESSURE SULFURIC ACID LEACH PROCESS

The physical characteristics of nodule reject waste material from the high-temperature and high-pressure sulfuric acid leach process should be similar to the nickel laterite tailings generated at Moa Bay, Cuba. These wastes settle to relatively high densities and become mechanically stable. As noted in the previous section, the major difference between the laterite tailings and the nodule reject waste material is the iron and manganese content. This iron-to-manganese ratio should have little effect on the physical properties. Expected physical characteristics of the tailings are a particle size of minus 200 mesh, settling densities of 40 to 50 pct solids, and good long-term stability.

REDUCTION AND HYDROCHLORIC PROCESS ACID LEACH

The physical characteristics of nodule reject waste material from the reduction and hydrochloric acid leach process has no known existing mineral processing analog. Based on very limited information, a particle size of less than 270 mesh and settling densities of 30 to 50 pct with fair long-term stability are anticipated. This material should be a hydroxide sludge with acid insoluble silicates such as clays and feldspars. Because of the chloride concentration of the waste, the possibility of rainwater leaching is increased.

SMELTING AND SULFURIC ACID LEACH PROCESS

The physical characteristics of the nodule reject waste material (slags and tailings) from the smelting and sulfuric acid leach process should be similar to wastes generated by nonferrous smelters. These wastes are generally large, inert, glassy materials that contain the elements sealed in an impermeable glass matrix. These slags are used for fill material and road beds among other uses. The physical parameters of nodule smelting slags should be similar to the preceding description with particle sizes generally greater than 10 mesh, excellent settling densities, and excellent long-term stability.

CHEMICAL CHARACTERISTICS

The predicted chemical characteristics are divided into four groups. The gas reduction and Cuprion ammoniacal leach processes are combined in one group as the compositions of these reject waste materials are expected to be similar. The remaining three processes are described separately. Also presented with the gas reduction and Cuprion sections are results of analyses of pilot plant-generated Cuprion reject waste material. The results of the EP toxicity test on this same material are also presented.

GAS REDUCTION AND CUPRION AMMONIACAL LEACH PROCESSES

Chemical characteristics of these nodule reject waste materials should be similar to those of nickel laterite tailings from the Caron process but with a higher manganese and lower iron content. Table 4 lists the 16 elements of interest, their estimated concentration ranges, and the probable compound forms expected to be present. The principal constituent of the waste will be manganese as manganese carbonate, hydroxide, and/or oxide. The other major constituent would be iron hydroxide. These two elements and their compounds should account for over 80 pct of the tailings composition. The principal anion forms for this waste material would be carbonate ($CO_3^{=}$) and hydroxide (OH^-) with some oxides present. Also present will be unreacted accessory minerals such as clays, feldspars, and silica.

Table 5 lists the results of the chemical analysis of a Cuprion pilot plant-generated reject waste material, and compares well with the predicted compositions listed in table

Table 4.—Predicted chemical composition of manganese nodule reject waste material from leach processes

Element	Remaining in tailings, pct	Estimated concentration range, wt-pct	Probable constituents present	Remaining in tailings, pct	Estimated concentration range, wt-pct	Probable constituents present
	Gas reduction and Cuprion ammoniacal leach			High-temperature and high-pressure sulfuric acid leach		
Antimony	~90	0.002 - 0.008	Iron or manganese antimonide.	~50	0.001 - 0.003	Iron or manganese antimonide.
Arsenic	~90	.003 - .010	Iron or manganese arsenate.	~90	.003 - .010	Iron or manganese arsenate.
Barium	~10	.150 - .300	$BaSO_4$	~100	.150 - .300	$BaSO_4$
Beryllium	~90	.0005- .0010	$BeCO_3$, BeO	~90	.0001- .0002	$BeSO_4 \cdot 4H_2O$, BeO
Cadmium	~90	.0001- .0020	$CdCO_3$, $Cd(OH)_2$	<1	<.0005	$CdSO_4$
Chromium	~90	.0010- .0020	Cr_2O_3, $Cr(OH)_3$	~90	<.0010- .0020	Cr_2O_3, $Cr_2(SO_4)_3$
Cobalt	~30	.050- .150	$Co(OH)_2$, $CoCO_3$	~33	.050 - .150	CoO
Copper	~10	.050 - .150	$Cu(OH)_2$, $CuCO_3$	~5	.002 - .008	CuO, $Cu(OH)_2$
Iron	~100	5.0 -10.0	$Fe(OH)_3$, $FeCO_3$, $Fe(OH)_2$, FeO·OH	~100	6 -10	Fe_2O_3, $Fe(OH)_3$, $KFe_3(SO_4)_2(OH)_6$
Lead	~90	.020 - .050	$PbCO_3$, $Pb(OH)_2$	~100	.03 - .06	$PbSO_4$
Manganese	~100	25 -35	$MnCO_3$, $Mn(OH)_2$, MnO, MnO_2	~95	25 -35	MnO_2, MnO
Molybdenum	~30	.01 - .02	Mo_2O_3, $(NH_4)_2MoO_4$?	~100	.04 - .06	Mo_2O_3
Nickel	~10	.15 - .30	$Ni(OH)_2$, $NiCO_3$	~5	.10 - .20	NiO
Selenium	~90	.0025- .0050	Iron or manganese selenate.	~90	.0025- 0050	Iron or manganese selenate.
Thallium	~70	.01 - .02	$Tl(OH)_3$	~80	.01 - .02	$Tl_2(SO_4)_3$
Zinc	~60	.075 - .125	$Zn(OH)_2$	~10	.01 - .03	$Zn(OH)_2$, ZnO
	Reduction and hydrochloric acid leach			Smelting and sulfuric acid leach		
Antimony	~10	0.0005- 0.0020	Iron antimonides.	~20	0.001 - 0.002	Iron antimonides.
Arsenic	~10	.0005- .0020	Iron arsenates.	~10	.002 - .004	Iron arsenates.
Barium	~10	.015 - .030	$BaSO_4$	~100	.30 - .50	BaO
Beryllium	~1	<.0001	BeO	~10	<.0001- .0001	BeO
Cadmium	~1	<.0005	$CdCl_2$	~50	.001 - .002	Cd, CdO, CdS
Chromium	~90	.001 - .002	Cr_2O_3, $CrCl_3$	~50	.001 - .003	Cr, Cr_2O_3
Cobalt	~1	.002 - .004	$CoCl_2$	~10	.04 - .06	Co, CoO, CoS
Copper	~1	.01 - .02	$Cu(OH)_2$, $CuCl_2$	~10	.10 - .30	Cu, CuO, CuS
Iron	~100	6 -10	$Fe(OH)_3$	~30	3 - 5	Fe, FeO
Lead	~10	.003 - .006	$PbCl_2$, PbO	~1	.001 - .005	Pb, PbO, PbS
Manganese	~5	1 - 2	MnO_2, $MnCl_2$	~5	2 - 4	Mn, MnO
Molybdenum	~1	.0005- .0010	Mo_2O_3	~10	.002 - .005	Mo_2O_3
Nickel	~1	.01 - .02	$NiCl_2$	~5	.10 - .15	Ni, NiO, NiS
Selenium	~10	.0005- .0020	Iron selenates.	~10	.0005- .0020	Iron selenates.
Thallium	~50	.005 - .015	$Tl(OH)_3$	~50	.01 - .02	Tl_2O_3
Zinc	~1	.001 - .002	$ZnCl_2$	~1	.005 - .01	Zn, ZnO, ZnS

Table 5.—Chemical composition of Cuprion pilot plant-generated reject waste material, weight-percent

Element	Concentration wt-pct
Antimony	0.004
Arsenic	.005
Barium	.004
Beryllium	.0005
Cadmium	.003
Chromium	.005
Cobalt	.18
Copper	.14
Iron	6
Lead	.050
Manganese	32
Molybdenum	.02
Nickel	.25
Selenium	.0001
Thallium	.016
Zinc	.11

Table 6.—EP toxicity results on Cuprion pilot plant-generated reject waste material, concentration, micrograms per milliliter

Element	Maximum allowed	Amount leached
Arsenic	5.0	0.004
Barium	100.0	4.4
Cadmium	1.0	.06
Chromium	5.0	.14
Lead	5.0	.6
Mercury	.2	.019
Selenium	1.0	.002
Silver	5.0	<.3

4. X-ray diffraction showed $MnCO_3$ as the principal compound.

Table 6 gives the results of the EP toxicity test on this same material. All of the elements are well within the limits as outlined by EPA (*4-5*).

HIGH-TEMPERATURE AND HIGH-PRESSURE SULFURIC ACID LEACH PROCESS

Chemical characteristics of this nodule reject waste material should be similar to those of tailings from laterite processing at Moa Bay, Cuba, but have a higher manganese and lower iron content. Table 4 lists the 16 elements of interest, their estimated concentration ranges, and the probable compound forms that may be present.

The major constituent in this waste should be manganese as manganese dioxide or oxide together with iron hydroxide. These two elements and their compounds account for over 80 pct of the tailings composition. The principal anion forms are hydroxide, oxide, and sulfate. Also present will be the unreacted accessory mineral phase constituents such as clays, feldspars, and silica.

REDUCTION AND HYDROCHLORIC ACID LEACH PROCESS

The chemical characteristics of nodule reject waste material from this process will be different from any of the other processes. Table 4 lists the 16 elements of interest, their estimated concentration range, and the probable compounds that could be present. The largest constituent of this waste material should be the acid insoluble fraction of the nodules; clays, feldspars, and silica. The remainder should

be iron hydroxide, other hydroxides, and entrained chloride salts not removed during the washing and filtration steps. The principal anion forms for the reject waste material should be silicate, hydroxide, and chloride.

SMELTING AND SULFURIC ACID LEACH PROCESS

The chemical characteristics of this nodule reject waste material (slags and tailings) will be similar to slags and tailings produced by nonferrous smelting processes. Table 4 lists the 16 elements of interest, their estimated concentrations, and the probable compound forms that may be present.

The major constituents of this material would be silicate glass and iron. The leach residues (about 1 pct of the total material) should contain trace levels of metal sulfides not leached during processing. Most elements present in the slag will exist in the metallic state or as oxides. Only a small amount of sulfides will be present from the leached residue.

SUMMARY AND CONCLUSIONS

As part of the Bureau work on analysis and characterization of manganese nodule processing rejects, the physical and chemical composition of the reject waste materials from potential manganese nodule processing are estimated. These reject waste materials are based on five process flowsheets: the gas reduction and ammoniacal leach process, the Cuprion ammoniacal leach process, the high-temperature and high-pressure sulfuric acid leach process, the reduction and hydrochloric acid leach process, and the smelting and sulfuric acid leach process. In these five processes only three lixiviants are used: ammonium-ammonium carbonate, sulfuric acid, and hydrochloric acid. Other lixiviants, such as nitric acid, are being considered, but the three discussed for the five processes are the most feasible for first-generation manganese processing.

The physical characteristics of the tailings were predicted based on limited available information on laterite processing.

Based on limited information, wastes from the gas reduction and Cuprion ammoniacal leach processes should have moderately high settling densities (50 to 60 pct), be minus 200 mesh, and have good long-term stability. The high-temperature and high-pressure sulfuric acid process wastes should be similar to wastes from the ammoniacal processes. The reduction and hydrochloric acid process would have somewhat lower settling density (30 to 50 pct), be about minus 270 mesh, and have only fair long-term stability. Wastes from the smelting and sulfuric acid process would be primarily glassy, inert slags at >10 mesh with excellent long-term stability.

The chemical characteristics were predicted based on the major lixiviant used and the process conditions. Estimates of the concentration of 16 elements in the reject waste material and the compounds present are presented, as well as estimates of the percentage of original feed remaining after processing.

Results of the EPA EP toxicity test on a pilot plant-generated reject waste material from the Cuprion process were well below maximum limits for designation as hazardous by EP toxicity.

All estimates and predictions are made based on no manganese recovery in the two ammoniacal processes and the high-temperature and high-pressure sulfuric acid process. If recovery and purification of manganese from these reject waste materials prove viable, then the physical and chemical characteristics of the wastes would be altered.

It appears that the reject waste material generated by the five outlined processes may have only minor environmental implications. Leachates from EP toxicity of the two ammoniacal leach wastes, the sulfuric acid leach waste, and the smelting leach waste should be well below maximum limits for classification as hazardous waste. Reject waste material from the hydrochloric acid leach process may have difficulties staying below EP toxicity limits because of soluble chloride salts.

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